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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

A Process for the Purification of Highly Dispersed Oxides of Silicon, Aluminium, Titanium and/or Zirconium

We DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER of 9 Weissfrauenstrasse, Frankfurt (Main) 1, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the purification of highly dispersed oxides, oxide mixtures and mixed oxides of silicon, aluminium, titanium and/or zirconium, which have been obtained by pyrogenic decomposition and contain impurities originating from their production, and to an apparatus for use in the process.

It is known to produce highly dispersed oxides by reacting the above metals or metalloid or their volatile compounds in vapour form at relatively high temperatures in the presence of substances or mixtures of substances having a hydrolysing and/or oxidising action. The metals or metalloid which are to be reacted, or their volatile compounds, more especially their halides, may, for example, be reacted in the gas phase with steam or gas mixtures generating steam. The oxides are formed as aerosols and are thereafter isolated at temperatures below the dew point of the gaseous reaction products which can easily be condensed. In this case, the steam-forming gas mixture can consist of combustible gases which more especially contain or form hydrogen and of incombustible gases, advantageously containing oxygen. The oxides are formed with a particle size smaller than 150 millimicron. It is particularly advantageous to use as starting materials the volatile halides, more especially the chlorides of the metals or metalloid. It is also possible simultaneously to start from two or more metals or one or more metals and the metalloid, or their volatile compounds, and to supply these together for the thermal decomposition, so that the oxides are separated out in the form of mixed oxides. Furthermore, it is possible for the various oxides which can be obtained to be subsequently combined with one another for the production of oxide mixtures.

If starting materials containing halogen, more especially silicon tetrachloride, are used for the thermal decomposition, then products are obtained which, because of their high absorption power, contain relatively large quantities of hydrogen halide and also halogen directly bonded to the metal or metalloid atom. Such oxides have a strong acid reaction. Their content of hydrohalic acid can for example be 0.1%, so that a pH-value of about 1.8 is produced. The pH can be determined on a sample of 4g. of the oxide in 100 ml. of water by means of a glass electrode. This makes the products unsuitable for many purposes. In order to deacidify the oxides, the oxides have hitherto been subjected to a heat treatment at temperatures from 200 to 500° C., in some cases in a current of gaseous and/or vaporous media. Steam has also been used for this purpose and the treatment has always been carried out in a rotary tube or on an endless steel band or in a worm-type conveyor. In order to achieve a deacidification to achieve a pH-value of 4.0, this treatment had to be carried out for a period of about 8 to 10 minutes. An important disadvantage with this treatment was that it was always neces-

sary to use apparatus having mechanically moving parts which apparatus was very liable to breakdown at the working temperature of about 500° C. This resulted in frequent interruptions for the maintenance of the apparatus. In addition, this process involves a considerable expenditure for energy.

The present invention provides a process for removing halogens and/or halogen hydride from highly dispersed oxides, oxide mixtures or mixed oxides of silicon, aluminium, titanium and/or zirconium which have been obtained by vapour-phase hydrolysis or oxidation of halides of these elements in vaporous state in the presence of gases or vapours having a hydrolysing and/or oxidising action, and if desired, in the presence of an inert gas, at elevated temperatures which comprises introducing the highly-dispersed oxides, oxide mixtures or mixed oxides into a treatment chamber in parallel with a stream of steam which may be diluted with an inert gas so as to form a turbulent suspension of oxides in the steam, which suspension is heated at a temperature from 450 to 1000°C. and removing the treated oxides and the resultant gases containing impurities from the end of the treatment chamber opposite to the end at which they were introduced. Preferably the oxides are heated inside a treatment chamber to a temperature from 500 to 650°C., if halides other than fluorides have been used and at 700 to 800°C. if fluorides have been used.

Advantageously, the turbulent suspension in a stream of steam, is passed in an upward direction. It is of course possible in this case for the purifying treatment to be repeated several times. The simple oxides are preferably used in this process.

An important factor for the successful purification of the oxides or the oxide mixtures or mixed oxides is that the solid particles themselves should be brought to the above mentioned temperatures. How long they are kept at these temperatures depends substantially only on the required purity or quality of the final products. The purification is complete after a few seconds or minutes when using heating means having an intensive action. On the other hand, if heating arrangements which are less effective are used, the residence time of the particles must be correspondingly lengthened. An effective heating of the treatment chamber and thus an effective and rapid purification of the oxides can often not be achieved in a satisfactory manner by external heating, as shown by our own experiments, especially when the process is carried out on an industrial scale. The manner in which the necessary temperatures are produced is *per se* not critical within the scope of the present invention. However, the use of an internal heating system, advantageously with simultaneous supply of hot air, is always advantageous as regards energy consumption. The internal heating can be produced in a manner known *per se* by infra-red radiators, by high frequency fields or by a flame burning in the treatment chamber. Internal heating by electric heater elements which are arranged in an insulating material, for example in quartz tubes, is preferred on account of the good efficiency and resistivity of such elements with respect to the reaction medium. The so-called "heating lances" which can easily be arranged in relatively large number inside the treatment chamber, have proved especially suitable.

The purification of those oxides or oxide mixtures or mixed oxides which contain fluorine or fluorine compounds as impurities, because they have been produced with the use of silicon tetrafluoride as starting material, should be effected in the upper range of the indicated temperature limits, i.e. at 700 to 800° C., while with all other impurities, it is not necessary to exceed a temperature of about 700° C. and, in order to avoid structural changes at the surface of the oxide particles, this in fact is not advisable. Since it is of decisive importance for successfully carrying out the process that the particles to be treated are themselves brought to the indicated temperatures, it is necessary in certain cases to provide for a sufficiently long residence time of these particles in the treatment chamber. For example, in the aforementioned case, the purification of those oxides which contain fluorine or fluorine compounds is for example carried out with a residence time of 4 to 5 minutes and at temperatures from 100 to 800° C. With shorter residence times, for example those from 1 to 2 seconds, it is advisable with these oxides for the temperature of the turbulent suspension to be raised to 900° C. or better still to about 1000° C.

The steam which is used can, if desired, be diluted with an inert gas, such as air or nitrogen. By this means it is possible to regulate the steam partial pressure in the treatment chamber. The adjustment of partial pressure can be varied within wide limits and depends only on the actual requirements for the production of products having a certain quality. Generally speaking, it is advisable not to use saturated steam.

Furthermore, it is essential for successfully carrying out the process that the waste gases containing the impurities are constantly extracted, that is to say, they must be separated from the solid particles before the oxides are cooled to those temperatures at which an appreciable re-absorption, of the impurities takes place.

It is particularly advantageous for the process according to the invention to be carried out continuously.

The treatment is advantageously carried

out in a treatment chamber which is of such dimensions that the turbulent suspension constantly travels upwardly and can constantly discharge from the upper part of the chamber, advantageously after passing through a steadying zone. The waste gases are also extracted in the upper part of the treatment chamber. A steadying zone can be achieved in simple manner by an enlargement of the furnace cross-section. This method is especially suitable for fully continuous operation.

The oxides are advantageously fed together with the steam into the treatment chamber and are thus constantly in turbulent motion when they leave the chamber and also in relative movement to the steam. Considered as a whole, however, they constantly move towards the upper outlet opening of the treatment chamber. When carrying out the process according to the invention, it is essential that the oxides to be treated have particles small enough for them to be suspended and flow upwardly in the stream of steam. When using highly dispersed oxides, which are obtained with a particle size smaller than 150 millimicron, it was very surprising that it was possible to bring about such a turbulent motion and a subsequent separation of the solid particles from the supporting medium. This applies more especially when carrying out the unidirectional flow process. It was also surprising that a successful treatment could be carried out in extremely short times.

The velocity at which the particles to be treated flow through the treatment chamber must at least be sufficiently high for the flow conditions to be satisfied. With the treatment of highly dispersed oxides, this is the case when a flow velocity of the supporting medium of about 2.0 cm./sec. is reached. The setting of a predetermined velocity can be effected in simple manner by the choice of suitable dimensions of the treatment chamber and/or of the quantity of steam or gas to be supplied.

Furthermore, it is advisable that hot air or another hot inert gas should concurrently be used, in addition to the steam and in such a way that the hot air at least partially supplies the heat quantity required for the treatment. The hot air is preferably supplied together with the steam to the treatment chamber. This can for example be effected by spraying water by means of a proportioning pump into an air heater.

A particularly advantageous embodiment of the process provides for coupling the generation of steam and heat. This can for example be effected by one or more oxyhydrogen gas flames.

If the process according to the invention is carried out with the use of hot air, this can simultaneously be used for pneumatically conveying the oxides which are to be treated, by both being introduced from below into the treatment chamber and by the steam preferably being simultaneously admixed therewith. This conveying of the oxides to be treated by pneumatic means is particularly desirable for regulating the residence times in the treatment chamber. It has surprisingly been found in this case that it is possible to work with relatively small quantities of air, so that quite a small heat supply is sufficient.

It was quite surprising that the previously described treatment of oxides of extraordinarily finely divided form, which assume very large volumes in the turbulent condition, can be carried out in a turbulent suspension. It was also surprising that the purification with steam, for which formerly residence times of 8 to 10 minutes were required, can for example be carried out with residence time of only 20 seconds, and likewise a pH-value of the final product of 4.0 to 4.3 is adjusted. An advantage which is important with the process according to the invention is that a thorough purification can be achieved with a low energy consumption and that it is possible in this connection to use apparatus which does not comprise any mechanically moving parts. It is also possible to use for the apparatus ceramic materials instead of metals whereby once again a higher purity of the products is guaranteed. Furthermore, it is advantageous and important that the grit formation is considerably reduced in the process according to the invention and that the separation of the grit does not have to be carried out by special means but can be effected by a simple periodic discharge at the lower end of the treatment chamber, for example by opening a valve.

One apparatus which has proved to be particularly suitable for carrying out the process is illustrated in the accompanying drawings.

Referring now to Fig. 1 of the accompanying drawings, the apparatus consists of a vertically disposed tubular furnace 1 with supply members 5 for the oxides, the steam and the air and a funnel-shaped enlargement 2 at its upper end, which serves as a steadying zone, and a discharge 3 for the treated ovides and also a discharge 4 for the waste gases. Finally, an additional gas heating arrangement 7 can be provided with this apparatus. A device for separating out the grit can be provided at the lowest point of the reaction tube.

Air is supplied through pipe 8 to an air heater 9. The necessary quantity of water required is supplied to the heater through pipe 10 at the same time, the oxide coming from supply vessels 12 is fed into pipe 11 by way of bucket wheel lock chambers or even by a gravity feed device. The mixture being formed ascends in a turbulent suspension in the tubular part of the furnace 1.

The purification is carried out therein under the influence of the high temperature. From the steady zone 2, the treated oxide passes to the discharge device 3. It is possible with advantage for a cyclone also to be arranged above the steadying zone.

The reaction chamber is of course not restricted to the cylindrical form; other shapes, for example that of a conical casing, are possible. The reaction chamber should preferably be insulated against heat dissipation.

For the internal heating, one embodiment which has proved especially suitable is that which is shown in Figures 2 and 3 of the accompanying drawing. In this embodiment rod-shaped or tubular heating members 6 which are preferably operated by electric current are arranged inside the tubular furnace substantially perpendicularly of its longitudinal axis. These heating members are preferably so arranged that they are always offset by about 60° relatively to one another in their longitudinal axis.

The invention is further illustrated by the following Examples. In these Examples the pH is determined by means of a glass electrode using a suspension of 4g. of oxide in 100 ml. of water.

EXAMPLE 1.

28 kg. of highly dispersed silica with a pH-value of 1.8 are fed together with 4.5 cubic metres of steam and 5 cubic metres of compressed air at a pressure of about 1 atmosphere hourly into an apparatus which corresponds to that shown in Figure 1 and which has a fluidised bed volume of 100 litres. The compressed air is heated beforehand to 140° C. in an air heater. Inside the furnace, a temperature of 520 to 570° C. is maintained by means of an electrical internal heating system. The flow velocity of the turbulent suspension is 10 to 12 cm./sec., and the total residence time 90 seconds. The weight by volume of the silica in the furnace is 7 to 8 g./l. After leaving the furnace, the silica has a pH-value of 4.0.

EXAMPLE 2.

28 kg. of highly dispersed silica produced from silicon tetrafluoride as starting material and with a pH-value of 2.0, corresponding to a fluorine content of 5 to 6%, are introduced every hour, together with 4.5 cubic metres of steam and 5 cubic metres of compressed air at 1 atm., into an apparatus which is shown in Figure 1. The fluid bed has a volume of 300 litres. The design thereof corresponds substantially to the apparatus shown in Fig. 1 except that the cylindrical part is increased to three times the size. Inside the furnace, a temperature of 750—800° C. is maintained by means of an electrical heating system. The flow velocity of the turbulent suspension is 8 to 10 cm./sec., and the residence time is 4 to 5 minutes. The weight by volume of the silica in the furnace is 7 to 8 g./l. After leaving the furnace, the silica, has a pH-value of 3.8.

WHAT WE CLAIM IS:—

1. A process for removing halogens and/or halogen hydride from highly dispersed oxides, oxide mixtures or mixed oxides of silicon, aluminium, titanium and/or zirconium which have been obtained by vapour-phase hydrolysis or oxidation of halides of these elements in vaporous state in the presence of gases or vapours having a hydrolysing and/or oxidising action, and if desired, in the presence of an inert gas, at elevated temperatures which comprises introducing the highly-dispersed oxides, oxide mixtures or mixed oxides into a treatment chamber in parallel with a stream of steam which may be diluted with an inert gas so as to form a turbulent suspension of oxides in the steam, which suspension is heated at a temperature from 450 to 1000°C. and removing the treated oxides and the resultant gases containing impurities from the end of the treatment chamber opposite to the end at which they were introduced.

2. A process as claimed in claim 1 wherein when the oxides have been produced from halides other than fluoride the turbulent suspension is heated at 500 to 650°C., and when they have been produced from fluorides, the suspension is heated at 700 to 800°C.

3. A process as claimed in claim 1 or 2, wherein the purification is carried out continuously.

4. A process as claimed in any of claims 1 to 3 wherein the treatment is carried out in a treatment chamber which is of such dimensions that the turbulent suspension constantly travels upwardly and constantly discharges from the upper part of the chamber, preferably after passing through a steadying zone, while the waste gases are likewise extracted in the upper part of the chamber.

5. A process as claimed in any of claims 1 to 4, wherein the heat required for the treatment is partially supplied in the form of hot air, advantageously together with the steam.

6. A process as claimed in any of claims 1 to 5, wherein the temperature is adjusted by means of an internal heating system, advantageously together with a supply of hot air.

7. A process as claimed in any of claims 1 to 6, wherein the steam necessary for the treatment and the requisite heat is wholly or partially produced by one or more oxy-hydrogen gas flames.

8. A process as claimed in any of claims 1 to 7 wherein the hot air is simultaneously used for pneumatically conveying the oxides to be treated.

9. A process as claimed in claim 1 which is carried out in an apparatus comprising a

vertically-disposed tubular furnace with supply members for oxides, steam and air and a funnel-shaped enlargement disposed at its upper end, which enlargement comprises a discharge for the treated oxides and an outlet for the waste gases.

10. A process as claimed in claim 9 wherein rod-like or tubular heater elements which are advantageously offset by 60° relatively to one another in their longitudinal axis are, disposed inside the tubular furnace substantially at right-angles to the longitudinal axis of the furnace.

11. A process as claimed in claim 1 which is carried out in an apparatus substantially as described with reference to the accompanying drawings.

12. A process as claimed in claim 1 substantially as described with reference to either of the Examples.

13. Oxides, mixed oxides and oxide mixtures of silicon, aluminium, titanium and/or zirconium freed from halogens and/or halogen hydrides by the process claimed in any of the preceding claims.

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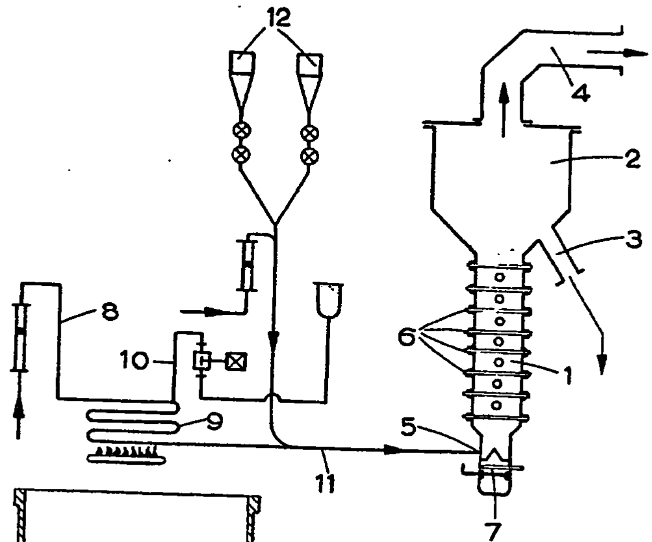
1003957 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 1.



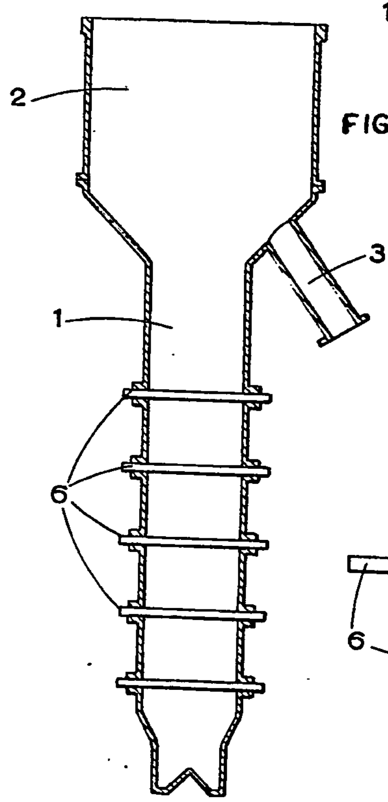


FIG. 3

FIG. 2.